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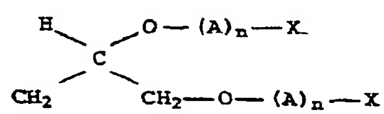
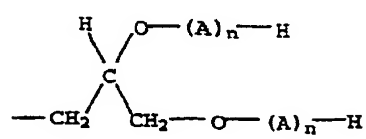
(54) Title: ZWITTERIONIC POLYAMINES AND A PROCESS FOR THEIR PRODUCTION

$(A)_n\text{-}X$ (I)



(II)

$—(A)_n—H,$ (a)



(b)

(57) Abstract: A zwitterionic polyamine comprising a crosslinked polyamine backbone having 2 to 12 tertiary or quaternary amino nitrogen atoms and a weight average molecular weight of from 150 to 1,500 wherein the crosslinked polyamine backbone is obtained by reacting (i) an aliphatic or araliphatic monoamine or a polyamine containing 2 to 5 primary, secondary or tertiary nitrogen groups with (ii) a crosslinker selected from the group consisting of epihalohydrins, polyglycidyl ethers with 2 to 4 glycidyl groups, polyhalohydrins with 2 to 4 halohydrine groups, dicarboxylic acids, their esters chlorides, amides or anhydrides, diisocyanates, urea and melamine, where at least one tertiary amine and group of the crosslinked polyamine backbone contains at least two groups having formula (I) or (II) wherein A is an alkylene oxide unit or tetrahydrofuran unit, n is a number of from 1 to 50 and X is an anionic group, or contains one group of formula (I) or (II) and one group selected from radicals consisting of (a), (b), C_1- to C_{22}-alkyl and C_7- to C_{22}-aralkyl, the meaning of A and n is the same as in formula (I) or (II) and a process for the production of said zwitterionic polyamines. The zwitterionic polyamines are used as additives in detergents.

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Zwitterionic polyamines and a process for their production

Description

The present invention relates to zwitterionic polyamines and a process for their production by alkoxylation of polyetherpolyamines and introduction of anionic groups.

Background of the invention

EP-A-0111976 and EP-A-0112592 relate to zwitterionic polymers which are for example obtained by alkoxylation of polyalkyleneamines such as triethylenetetramine or tetraethylenepentamine or of polyethyleneimines, sulfonation of the alkoxylated products and subsequent quaternization. These zwitterionic products have clay-soil removal and anti-redeposition properties when used in detergent compositions, however their effectiveness in dispersing and removing clay embedded in the fabric into the laundry liquor is not sufficient. Furthermore it was found, that preferred embodiments of the above mentioned patents show thermal instability.

U.S. Patent 4,739,094 discloses alkoxylated aminopolyethers containing units of ethylene oxide and propylene oxide and having a molecular weight of from 10,000 to 150,000. The alkoxylated aminopolyethers are water-soluble and are used in 5 to 60 % strength by weight aqueous solution in the preparation of coal/water slurries. If appropriate, the alkoxylated aminopolyethers can also be reacted with carboxylic acid anhydrides, amidosulfonic acids and urea, acid chlorides of sulfur or of phosphorus or chloroacetic acid esters. The reaction products can be converted into ionic compounds by subsequent neutralization or hydrolysis.

In the course of optimizing modern laundry detergents there is a need to improve properties of clay soil removal agents for better effectiveness in the wash liquour, improved synergy with the surfactant system and for better thermal stability during processing and storing.

It is therefore an object of the invention to provide new polymers with improved thermal stability.

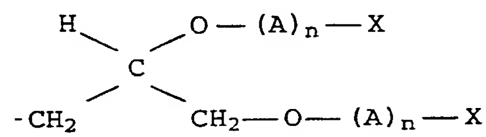
Summary of the invention

The above object is achieved with a zwitterionic polyamine comprising a crosslinked polyamine backbone having 2 to 12 tertiary or quaternary amino nitrogen atoms and a weight avarage molecular weight of from 150 to 1,500 wherein the crosslinked polyamine backbone is obtained by reacting

(i) an aliphatic or araliphatic monoamine or a polyamine containing 2 to 5 primary, secondary or tertiary amino nitrogen groups with

(ii) a crosslinker selected from the group consisting of epihalohydrins, polyglycidyl ethers with 2 to 4 glycidyl groups, polyhalohydrins with 2 to 4 halohydrine groups, dicarboxylic acids, their esters chlorides, amides or anhydrides, diisocyanates, urea and melamine,

in a ratio (i) : (ii) of from 20 : 1 to 1 : 1 with reference to molar amounts of amino groups in the amines of (i) and molar amounts of reactive groups in the crosslinker of (ii), at least one tertiary amine end group of the crosslinked polyamine backbone contains at least two groups having the formula

$-(A)_n-X$ (I) or  (II)

wherein

A means an ethylene oxide unit, a propylene oxide unit, a unit of butylene oxides and a tetrahydrofuran unit,

n is a number of from 1 to 50,

X is $-SO_3M$, $-CH_2-CH_2-SO_3M$, $-CH_2-CH_2-CH_2-SO_3M$,

$-CH_2-CH(OH)-CH_2-SO_3M$,

$-CH_2-COOM$, $-CH_2-CH_2-COOM$,

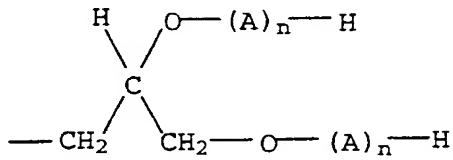
$-PO_3M_2$, $-CH_2-CH_2-PO_3M_2$,

with the proviso that in formula II one X may also be hydrogen and

M is hydrogen, alkali metal or ammonium,

or contain one group of formula I or II and one group selected from radicals consisting of

$-(A)_n-H$,



C_1- to C_{22}-alkyl and C_7- to C_{22}-aralkyl, the meaning of A and n is the same as in formula I or II,
and optionally contains up to 100% of the nitrogen atoms quaternized.

The object is also achieved with a process for the production of zwitterionic polyamines which comprises

(a) reacting

(i) an aliphatic or araliphatic monoamine or a polyamine containing 2 to 5 primary, secondary or tertiary nitrogen groups with

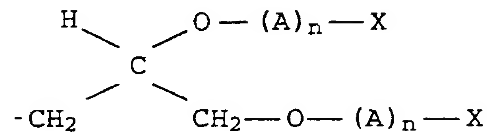
(ii) a crosslinker selected from the group consisting of epihalohydrins, polyglycidyl ethers with 2 to 4 glycidyl groups, polyhalohydrins with 2 to 4 halohydrine groups, dicarboxylic acids, their esters chlorides, amides or anhydrides, diisocyanates, urea and melamine,

in a ratio (i) : (ii) of from 20 : 1 to 1 : 1 with reference to molar amounts of amino groups in the amines of (i) and molar amounts of reactive groups in the crosslinker of (ii), resulting in the formation of a crosslinked polyamine having a molecular weight of from 150 to 1,500,

(b) alkoxylating the crosslinked polyamine obtained according to step (a) with at least one C2- to C4-alkylene oxide or tetrahydrofurane at such a ratio that on each NH group of the crosslinked polyamine 1 to 50 units of the alkylene oxide are added,

(c) reacting the alkoxylated polyamine obtained according to step (b) with a compound selected from the group consisting of halogen sulfonic acid, halogen phosphorous acid, vinyl sulfonic acid, propane sultone, halogen acetic acid, acrylic acid, methacrylic acid, vinyl phosphorous acid, and the alkali metal or ammonium salts of the said acids in such a manner that at least one ter-

tiary amine end group of the alkoxylated crosslinked polyamine contains two groups having the formula

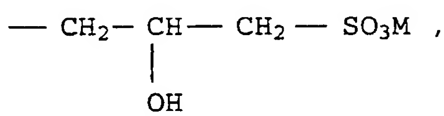
$-(A)_n-X$ (I) or  (II)

wherein

A means an ethylene oxide unit, a propylene oxide unit, a unit of butylene oxides and a tetrahydrofuran unit,

n is a number of from 1 to 50,

X is $-SO_3M$, $-CH_2-CH_2-SO_3M$, $-CH_2-CH_2-CH_2-SO_3M$,



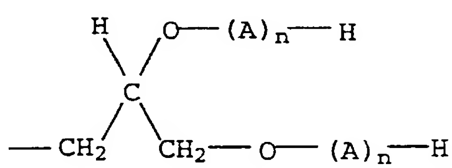
$-CH_2-COOM$, $-CH_2-CH_2-COOM$,

$-PO_3M_2$, $-CH_2-CH_2-PO_3M_2$,

with the proviso that in formula II one X may also be hydrogen and

M is hydrogen, alkali metal or ammonium,

or containing one group of formula I or II and one group selected from radicals consisting of

$-(A)_n-H$, 

C_1- to C_{22}-alkyl and C_7- to C_{22}-aralkyl, the meaning of A and n is the same as in formula I or II,

and optionally

(d) quaternizing up to 100% of the tertiary nitrogen atoms of the reaction product obtained according to step (c), or quaternizing the reaction product obtained according to step (b) and subsequently carrying out the reaction according to step (c).

Preferred zwitterionic polyamines contain two groups of formula I or II attached to the tertiary nitrogen atoms of the end groups of the crosslinked polyamine backbone. Especially preferred zwitterionic polyamines contain the nitrogen atoms of the end groups of the crosslinked polyamine backbone quaternized and, as substituents, two groups of formula I or II and one C1 to C22 alkyl group.

Of particular interest are such zwitterionic polyamines, wherein the nitrogen atoms of the end groups of the crosslinked polyamine backbone are quaternized and contain, as substituents, two groups of formula I and a C1 to C22 alkyl group. Other zwitterionic polyamines which are of particular interest are those wherein the nitrogen atoms of the end groups of the polyamine backbone are quaternized and contain, as substituents, two groups of formula I and a hydroxyethyl or a hydroxypropyl group.

The crosslinked polyamine backbone is obtained by reacting (i) an aliphatic or araliphatic monoamine or a polyamine containing 2 to 5 primary, secondary or tertiary amino nitrogen atoms with (ii) a crosslinker. As a result, polyamines having a molecular weight of from about 150 to about 1,500, preferably to about 1,200 are obtained. Suitable amines are for example primary C1- to C22-alkylamines, C7- to C22-aralkylamines, C6- to C22-cycloalkylamines, monohydroxy-C2- to C4-alkylamines, dihydroxy-C2- to C4-alkylamines trihydroxy-C2- to C4-alkylamines, linear or branched C2- to C12-alkylenediamines, C8- to C22-aralkylendiamines, C7- to C22-cycloalkylenediamines, α,ω-polyetherdiamines containing 1 to 10 alkoxy units between the nitrogen atoms and linear or branched polyalkylenepolyamines having 2 to 4 C2- to C12-alkyleneamine units.

Examples for the above groups of amines are methylamine, ethylamine, propylamine, butylamine, octylamine, 2-ethylhexylamine, benzylamine,

ethanolamine, 2-hydroxypropylamine, 2-hydroxybutylamine, diethanolamine, bis(2-hydroxypropyl)amine, bis(2-hydroxybutyl)amine, triethanolamine, tris(2-hydroxypropylamine), tris(2-hydroxybutylamine)

ethylenediamine. 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,3-diamino-3,3-dimethylpropane, piperazine, 4,9-dioxadodecanediamine-1,12, 4,7,10-trioxatridecanediamine-1,13, 4,11-dioxatetradecanediamine-1,14, α,ω-diaminopolyethyleneglycole with 2-10 ethyleneglycole-units, α,ω-diaminopolypropyleneglycole with 2-10 propyleneglycole-units, α,ω-diaminopolytetrhaydrofurane with 2-10 oxabutylene-units, Isophoronedimine, bis(4-aminocyclohexyl)methane, 1,3-diaminhyclohexane, 1,3-diamino-2-methylcyclohexane, 1,3-diamino-4-methylhyclohexane, o-di(aminomethylene)benzene, p-di(aminomethylene)benzene, m-di(aminomethylene)benzene

diethylenetriamine, dipropylenetriamine, N-(aminoethyl)propylendiamine, N,N-bis(aminopropyl)methylamine, N(aminoethyl)butylenediamine, N,N-bis(aminopropyl)butylamine, N,N-bis(aminopropyl)octylamine, N(aminoethyl)hexamethylendiamine, N-(aminopropyl)hexamethylendiamine, bishexamethylenetriamine, N-dimethylaminopropylethylendiamin, N-(2-aminoethyl)piperazin, N-(3-aminopropyl)piperazin

bis(aminoethyl)piperazine, bis(aminopropyl)piperazine, triethylentetramine, tetraethylenepentamine, N,N'-bis(aminopropyl)ethylendiamine), tripropylentetramine, N,N'-bis(aminopropyl)butylenediamine-1,4, N,N'-bis(aminoethyl)hexamethylendiamine, N,N'-bis(aminopropyl)hexamethylendiamine

Especially preferred amines are diethanolamine, bis-(2-hydroxypropyl)amine, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 4,9-dioxadodecanediamine-1,12, 4,7,10-trioxatridecanediamine-1,13, diethylenetriamine, dipropylenetriamine, bishexamethylenetriamine and bis(aminopropyl)piperazine.

Suitable crosslinkers, which contain at least two functional groups, are for example α-,ω- or vicinal dichloroalkanes having at least 4 carbon atoms such as 1,4-dichlorobutane and 1,6-dichlorohexane. Further suitable crosslinkers are glycidyl halides such as epichlorohydrin, bischlorohydrin ethers of polyols, polychlorohydrin ethers of polyols, bischlorohydrin ethers of polyalkylene glycols, chloroformic acid esters, chlorides of dibasic saturated dicarboxylic acids, phosgene and, in particular, halogen-free crosslinkers.

Preferably used crosslinkers are epichlorohydrin and bischlorohydrin ethers of ethylene glycol, polyethylene glycol having 2 to 20 especially 2 to 14 ethylene glycol units, propylene glycols, polypropylene glycols, copolymers of ethylene oxide and propylene oxide, butanediol-1,4, neopentyl glycol, hexanediol-1,6, resorci-

nol, glycerol, diglycerol and pentaerythritol. Other preferred crosslinkers are trischlorohydrinethers of trimethylolpropane, glycerol and pentaerythrithol and the reaction product 1 mole of pentaerythritol with 4 moles of epichlorohydrin. Halogen-free crosslinkers which are at least bifunctional are preferably selected from the group consisting of:

(1) melamine and/or urea,

(2) dibasic saturated carboxylic acids and also the esters, amides and anhydrides which are in each case derived therefrom,

(3) diepoxides, polyepoxides, α,ω-diisocyanates such as hexamethylene diisocyanate

and also mixtures of the said crosslinkers. Diepoxides and polyepoxide may be obtained from bischlorohydrinethers of alkylene glycols and polyethylene glycols or from tris and tetrachlorohydrinethers of polyols such as trimethylolpropane and pentaerythritol.

Examples of suitable halogen-free group (2) crosslinkers are dibasic saturated carboxylic acids, such as C_4-C_{12}-dicarboxylic acids, and also the salts, diesters and diamides which are derived therefrom. Examples of such acids are succinic acid, adipic acid, terephthalic acid, phthalic acid and α,ω-dodecanoic acid.

The esters of the dicarboxylic acids which come into consideration are preferably derived from alcohols having from 1 to 4 carbon atoms. Examples of suitable dicarboxylic acid esters are dimethyl succinate, diethyl succinate, diisopropyl succinate, di-n-propyl succinate, diisobutyl succinate, dimethyl adipate, diethyl adipate and diisopropyl adipate.

Examples of suitable dicarboxylic acid anhydrides are phthalic anhydride and succinic anhydride.

Preferred compounds of group (3) are bisglycidyl ethers of ethylene glycol, polyethylene glycol having 2 to 20 ethylene glycol units, propylene glycol, polypropylene glycol ethers, copolymers of ethylene oxide and propylene oxide, butanediol-1,4, neopentyl glycol, hexanediol-1,6 and resorcinol and diisocyanates such as hexamethylene diisocyanate.

It is also preferred to use mixtures of crosslinkers, for example,

– mixtures of diglycidyl ether of ethylene glycol with bischlorohydrin ether of ethylene glycol,

– mixtures of diglycidyl ether of polyethylene glycols having 2 to 20 ethylene glycol units with bischlorohydrin ethers of polyethylene glycols having 2 to 20 ethylene glycol units

Crosslinked polyamines are obtainable by reacting at least one compound of group (i) with at least one compound of group (ii). The reaction may be carried out in substance, in solution in an inert solvent or in dispersion in an aqueous medium or in an inert solvent.

Preferred zwitterionic polyamines are those wherein the crosslinked polyamine backbone is obtained by reacting

(i) an amine selected from the group consisting of diethanolamine, bis(2-hydroxypropyl)amine, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 4,9-dioxadodecanediamine-1,12, 4,7,10-trioxatridecanediamine-1,13, diethylenetriamine dipropylenetriamine, bis(hexamethylene)triamine and bis(aminopropyl)piperazine with

(ii) a crosslinker selected from the group consisting of epichlorohydrin, bischlorohydrinethers of C2- to C6- alkylene glycols, bischlorohydrinethers of polyethylene glycols having 2 to 14 ethylene glycol units, trischlorohydrinether of trimethylolpropane, trischlorohydrinether of glycerol, tetrachlorohydrinether of pentaerythritol, bisglycidylether of ethylene glycol, bisglycidylether of polyethylene glycols having 2 to 14 ethylene glycol units, trisglycidylether of trimethylolpropane, tetraglycidylether of pentaerythritol, urea, melamine, adipic acid, terephthalic acid, phthalic acid, α,ω-dodecanoic acid and hexamethylene diisocyanate.

The polyamine backbone is then alkoxylated. In the next step of the multistage process anionic groups are introduced into the alkoxylated crosslinked polyamine backbone with the result that a zwitterionic polyamine is formed . Thereafter the zwitterionic polyamine may optionally be quaternized. In case that quaternized zwitterionic polyamines are desired it is possible to carry out the quaternization step before introducing anionic groups. The alkoxylated crosslinked polyamine obtained according to step (b)

is quaternized up to 100% and subsequently reacted with an anion-introducing agent such as chlorosulfonic acid.

The weight average molecular weight Mw of the zwitterionic polyamines is up to 9,000, preferably of from 1,500 to 7,500 and more preferably of from 2,000 to 7,000. The zwitterionic polyetherpolyamines can be soluble or dispersible in water and aqueous or nonaqueous solvents or formulations. In one preferred embodiment of the present invention they are water-soluble.

The zwitterionic polyetherpolyamines are net anionic. Preferably the average number of anionic charges resulting from groups X exceeds the average number of cationic charges resulting from protonated or quaternized amine groups by a factor of more than 1.2, more preferred of more than 1.5, most preferred of more than 1.8.

The zwitterionic polyetherpolyamines of the invention are prepared in a multistage process. According to step (a) the crosslinked polyamine backbone is formed by reacting the compounds of groups (i) and (ii). According to step (b) of this process a crosslinked polyamine backbone having a molecular weight of from 150 to 1500, 2 to 10 nitrogen atoms and containing at least 2 primary or secondary amino nitrogen end groups is reacted with at least one C2- to C4-alkylene oxide or tetrahydrofurane at such a ratio that on each NH group of the polyamine 1 to 50, preferably 15 to 25 alkylene oxide units are added. Ethylene oxide and propylene oxide are the preferred alkoxylating agents. If a mixture of alkylene oxides is added to the amino nitrogen then the polymerized alkylene oxides may be present in statistical distribution or as blocks. For example one can add first 10 to 20 of ethylene oxide units per NH group in the crosslinked polyamine and then add 5 to 10 propylene oxide units or vice versa.

Most preferred ethylene oxide alone or a combination of 1-15% propylene oxide or 1-10% butylene oxide with 85-99, 90-99% ethylene oxide respectively are used. If a combination of ethylene oxide and propylene oxide or butylene oxide is used preferably the propylene oxide or butylene oxide is reacted first with the NH and OH-groups of the polyamine backbone and the ethylene oxide is added after that.

The above described procedure gives polyalkoxylated products which have groups of formula

$-(A)_n-H$, wherein A and n have the meaning given for formula I.

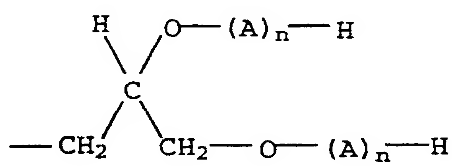
The polyamines are preferably ethoxylated in step (b) of the production of the zwitterionic polyetherpolyamines.

In order to produce zwitterionic polyamines having end groups of formula II a polyamine having a molecular weight of from 150 to 1500, 2 to 10 nitrogen atoms, containing at least 2 primary or secondary amino nitrogen groups and having up to 1 glycidol unit added per NH group is in step (b) of the process according to the invention alkoxylated at the OH groups and remaining NH groups as described above. The reaction of glycidol with said polyamine may be carried out to such an extent that at least 50 to 100% of the NH groups of the polyamine are substituted by one glycidol unit.

In step (c) of the production of the zwitterionic polyamines an anionic group is introduced into the alkoxylated crosslinked polyamines. This may be achieved by reacting the alkoxylated polyamines in a Michael type addition reaction with acrylic acid, methacrylic acid, vinyl sulfonic acid, vinylphosphonic acid or their alkalimetal or ammonium salts or by reacting them with halogen sulfonic acid, halogen phosphorous acid, propane sultone or halogen acetic acid. The preferred component for introducing anionic groups is chlorosulfonic acid.

Dependent on the amount of anionic agent used step (c) zwitterionic products are obtained which contain either two substituents of formula I or II or contain only one of them, if, for instance, only one mole of the anionic agent is used per one mole of OH end group of the alkoxylated polyamine. The non-reacted end groups of the alkoxylated polyamine may be characterized by a group selected from radicals consisting of

$-(A)_n-H$, and



the meaning of A and n is the same as in formula I or II.

The degree of substitution of the OH groups in the alkoxylated polyamines is such, that the finally resulting zwitterionic polyetherpolyamine is net anionic at the pH of intended use; e.g. from 40% up to 100% of the OH group are substituted by an anionic group. Preferably more than 60%, more preferred more then 80%, most preferred 90-100% of the OH-groups are substituted by an anionic group.

Moreover the zwitterionic polyetherpolyamines may also contain only one substituent of formula I or II and instead of the above described radicals a C_1- C_{22}-alkyl group or a C_7- to C_{22}-aralkyl group. Such compounds result when the polyamine used in the step (a) contains secondary amino groups having a C_1- to C_{22}-alkyl or a C_7- to C_{22}-aralkyl substituent.

The zwitterionic polyamines obtained in step (c) may optionally be reacted in a following step with a quaternizing agent. Alternatively, quaternized products may also be obtained by first quaternizing the reaction products obtained in step (b), i.e. the polyalkoxylated polyamines. Suitable quaternizing agents are for example C_1- to C_{22}-alkylhalides, C_7- to C22-aralkyl halides C_1-C_2-dialkylsulfates or alkylene oxides. Examples of quaternizing agents are dimethyl sulfate, diethyl sulfate, methylchloride, ethyl chloride, methyl bromide, ethyl bromide, butyl bromide, hexyl chloride, benzyl chloride, benzyl bromide, ethylene oxide or propylene oxide. Dialkylsulfates, C_1-C_4-alkylchlorides and benzoylchloride are preferred. Dimethyl sulfate is the most preferred quaternizing agent. Up to 100% of the tertiary nitrogen atoms of the zwitterionic polyetherpolyamine may be quaternized. If there is a quaternization step, then the degree of quaternization is, for example, 10 to 100%, preferably at least 25 % and more preferably 75 to 100%.

According to a preferred embodiment of the process for the production of zwitterionic polyamines the alkylene oxide is selected from the group consisting of ethylene oxide, propylene oxide, butylene oxide and mixtures of the said alkylene oxides. They are used in such an amount that on each NH group of the polyamine 15 to 40 units of the alkylene oxide are added.

The alkoxylated polyamine obtained is then reacted with chlorosulfonic acid in such ratio that at least one teritary end group of the polyamine contains two groups having the formula

$$-(A)_n-X \qquad \text{(I), wherein}$$

A is an ethylene oxide unit, a propylene oxide unit or a butylene oxide unit,
n is 15 - 40 and
X is SO_3H.

The zwitterionic reaction product is then quaternized with dimethyl sulfate, methyl chloride or benzyl chloride.

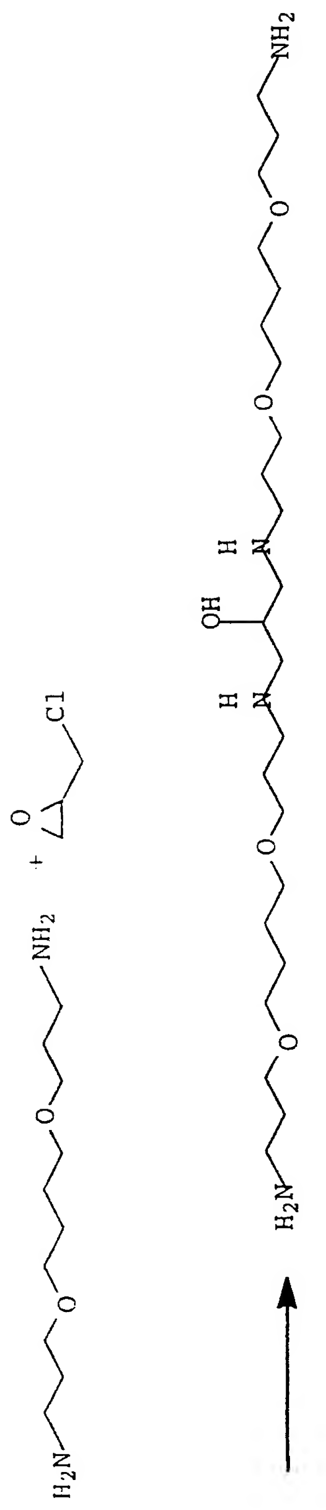
The alkoxylated polyamine may be quaternized up to 100 % before anionic groups are introduced by reaction with chlorosulfonic acid or another agent capable to introduce an anionic group. This procedure is preferred for the production of quaternized zwitterionic polyamines.

The zwitterionic polyamines are used as additive in laundry detergent compositions which provide enhanced hydrophilic soil, inter alia, clay, removal benefits. The new zwitterionic polyamines are especially useful in detergents comprising a surfactant system which comprises mid-chain branched surfactants inter alia mid-chain branched alkyl sulphonates. The zwitterionic polyamines are additionally used as effective dispersants for hydrophilic particles within aqueous and non-aqueous solutions and formulations.

The degree of quaternization and of sulfation was determined by ^{1}H-NMR. The amine number was determind by amine titration according to DIN 16 945.

Example 1

(a) Reaction of 4,9-dioxadodecane-1,12-diamine ("DODD") with epichlorohydrin ("Epi") according to the following equation



An aqueous solution of 1,428.0 g (7.0 mole) of 4,9-dioxadodecane-1,12-diamine in 1,509.0 g of water was placed under a blanket of nitrogen in a flask fitted with a stirrer, dropping funnel and a heating device. 80.9 g (0.875 moles) of epichlorohydrin were added under a stream of nitrogen to the aqueous solution within 20 minutes while stirring. The temperature of the reaction mixture was first 20°C and increased to 50°C. After the addition of epichlorohydrin was complete the reaction mixture was stirred at a temperature of 50°C for 21 hours under a stream of nitrogen. After this period of time no more epichlorohydrin could be detected.

In order to desalinate the reaction mixture 70.0 g (0.875 moles) of an aqueous sodium hydroxide solution was added while stirring. Water was removed at a rotary evaporator at a temperature of 90°C and thereafter by azeotropic destillation with toluene. The toluene was then removed and the residue treated with 600 ml of toluene at 90°C. The precipitated sodium chloride was filtered from the solution of the polyamine in toluene at 90°C. The reaction product had an amine number of 469.7 and a molecular weight Mw of 464 g/mole.

(b) Ethoxylation of the polyamine ("DODD/Epi 2:1") obtained according to (a)

232.3 g (0.5 moles) of DODD/Epi 2:1 and 12.3 g of water were placed in a pressurizable 5 l autoclave fitted with a stirrer. The autoclave was then sealed and three times pressurized with nitrogen at 5 bar. The pressure was released and thereafter the autoclave sealed presure-tight. The contents of the autoclave were heated while stirring to 110°C. At this temperature 136.4 g (3.1 moles) of ethylene oxide were added continuously while maintaining the temperature between 110 - 120°C and the maximum pressure up to 5 bar. The reaction mixture was stirred until the pressure was constant and then cooled to about 80°C. The pressure was then released, the autoclave three times pressurized with nitrogen at 5 bar and 11.5 g of a 50%strenght by weight sodium hydroxide solution were added.

The autoclave was then sealed and vacuum continuously applied to remove the water. The contents of the reactor were heated for four hours at 120°C and at a pressure of 10 mbar. Vacuum was removed with nitrogen and the autoclave heated to 140°C. Between 140 and 150°C 2,508 g (57 moles) of ethylene oxide were continuously introduced into the autoclave while stirring. The maximum pressure was 10 bar. The reaction mixture was stirred until the pres-

sure was constant. The contents of the reactor were then cooled to 80°C and the reactor three times pressurized with nitrogen at 5 bar. 2,880 g of a reaction product was obtained which was an ethoxylated DODD/Epi 2:1 containig 20 ethylene oxide units per NH group of the polyetherpolyamine ("DODD/Epi 2:1 EO20").

(c) Quaternization of the reaction product obtained according to (b)

Into a weighed, 2000ml, 3 neck round bottom flask fitted with argon inlet, condenser, addition funnel, thermometer, mechanical stirring and argon outlet (connected to a bubbler) is added DODD/Epi 2:1 EO20 (283.2 g, 0.295mol N, 98% active, Mw 5,000) and methylene chloride (1000g) under argon. The mixture was stirred at room temperature until the polymer has dissolved. The mixture was then cooled to 5°C using an ice bath. Dimethyl sulfate (39.5g, 0.31mol, , 99%) was slowly added using an addition funnel over a period of 15 minutes. The ice bath was removed and the reaction temperature was allowed to rise to room temperature. After 48 hrs. the reaction was complete. The degree of quaternization was about 90 % (determined by 1H-NMR). The molecular weight Mw of this product was 6,168 g/mole.

(d) Sulfation of the reaction product obtained according (c)

Sulfation of DODD/Epi 2:1 EO20 which was quaternized to about 90% of the product admixture was carried out under argon. The reaction mixture from the quaternization step (c) was cooled to 5°C using an ice bath (DODD/Epi 2:1 EO20, 90mol% quat, 0.59 mol OH). Chlorosulfonic acid (72g, 0.61 mol, 99%) was slowly added using an addition funnel. The temperature of the reaction mixture was not allowed to rise above 10°C. The ice bath was removed and the reaction temperature allowed to rise to room temperature. After 6 hrs. the reaction was complete. The reaction was again cooled to 5°C and sodium methoxide (264g, 1.22 mol, Aldrich, 25% in methanol) was slowly added to the rapidly stirred mixture. The temperature of the reaction mixture was not allowed to rise above 10°C. The reaction mixture was transferred to a single neck round bottom flask. Purified water (1300ml) was added to the reaction mixture and the methylene chloride, methanol and some water was stripped off on a rotary evaporator at 50°C. The clear, light yellow solution was transferred to a bottle for storage. The final product pH is checked and adjusted to ~9 using 1N NaOH or 1N HCl as needed. The degree of quaternization was about 90 % (determind by 1H-NMR).

Examples 2 - 7

According to the procedure given in Example 1 (a) the amines and the crosslinkers as well as their amounts specified below were used:

Example	Moles of amine	Amine	Moles of cross-linker	crosslinker
2	2	4,9-dioxadododeca-nediamine-1,12	1	butanediolbisglyci-dylether
3	2	hexamethylenedi-amine	1	epichlorohydrin
4	2	bis(hexa-methylen)diamine	1	epichlorohydrin
5	4	4,9-dioxadodecane-diamine	3	epichlorohydrin
6	2	diethanolamine	1	butanediolbisglyci-dylether
7	2	4,9-dioxadodecane-diamine-1,12	1	adipic acid

The above described crosslinked amines were ethoxylated according to the procedure given in Example 1 (b) to such a degree that 20 moles of ethylene oxide were added per mole of NH groups in the crosslinked polyamines. The ethoxylated products had the following amine number (measured according to DIN 16,945):

Example	Amine number
2	43.1
3	48.5
4	46.8
5	44.1
6	34.2
7	37.0

The ethoxylated crosslinked polyamines were then quaternized and subsequently sulfonated according to the procedures given in Example 1 (c) and (d). The reaction conditions were so adjusted that the degree of quaternization and of sulfonation was - with the exception of Example 6 - 90%. The degree of quaternization of the product of Example 6 was 90% and the degree of sulfation was 50 %.

Claims

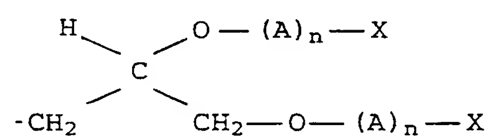
1. A zwitterionic polyamine comprising a crosslinked polyamine backbone having 2 to 12 tertiary or quaternary amino nitrogen atoms and a weight avarage molecular weight of from 150 to 1,500 wherein the crosslinked polyamine backbone is obtained by reacting

(i) an aliphatic or araliphatic monoamine or a polyamine containing 2 to 5 primary, secondary or tertiary amino nitrogen groups with

(ii) a crosslinker selected from the group consisting of epihalohydrins, polyglycidyl ethers with 2 to 4 glycidyl groups, polyhalohydrins with 2 to 4 halohydrine groups, dicarboxylic acids, their esters chlorides, amides or anhydrides, diisocyanates, urea and melamine,

in a ratio (i) : (ii) of from 20 : 1 to 1 : 1 with reference to molar amounts of amino groups in the amines of (i) and molar amounts of reactive groups in the crosslinker of (ii), at least one tertiary amine end group of the crosslinked polyamine backbone contains at least two groups having the formula

$-(A)_n-X$ (I) or



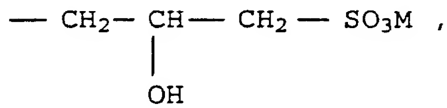
(II)

wherein

A means an ethylene oxide unit, a propylene oxide unit, a unit of butylene oxides and a tetrahydrofuran unit,

n is a number of from 1 to 50,

X is $-SO_3M$, $-CH_2-CH_2-SO_3M$, $-CH_2-CH_2-CH_2-SO_3M$,



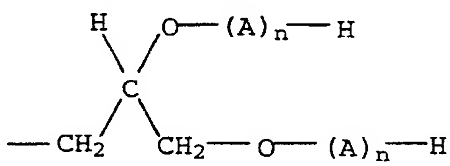
$-CH_2-COOM$, $-CH_2-CH_2-COOM$,

$-PO_3M_2$, $-CH_2-CH_2-PO_3M_2$,

with the proviso that in formula II one X may also be hydrogen and

M is hydrogen, alkali metal or ammonium,

or contain one group of formula I or II and one group selected from radicals consisting of

$-(A)_n-H$,  ,

C_1- to C_{22}-alkyl and C_7- to c_{22}-aralkyl, the meaning of A and n is the same as in formula I or II, and optionally contains up to 100% of the nitrogen atoms quaternized.

2. A zwitterionic polyamine as claimed in claim 1, wherein the tertiary nitrogen atoms of the end groups of the polyamine backbone contain two groups of formula I or II.

3. A zwitterionic polyamine as claimed in claim 1, wherein the nitrogen atoms of the end groups of the polyamine backbone are quaternized and contain, as substituents, two groups of formula I or II and one C_1- to C_{22}-alkyl group or a hydroxyalkyl group.

4. A zwitterionic polyamine as claimed in claim 1, wherein the nitrogen atoms of the end groups of the polyamine backbone are quaternized and contain, as substituents, two groups of formula I and a C_1- to C_{22}-alkyl group.

5. A zwitterionic polyamine as claimed in claim 1, wherein the nitrogen atoms of the end groups of the polyamine backbone are quaternized and contain, as substituents, two groups of formula I and a hydroxyethyl or hydroxypropyl group.

6. A zwitterionic polyamine as claimed in claim 1, wherein the crosslinked polyamine backbone is obtained by reacting

(i) an amine selected from the group consisting of diethanolamine, bis(2-hydroxypropyl)amine, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 4,9-dioxadodecane-diamine-1,12, 4,7,10-trioxatridecanediamine-1,13, diethylenetriamine dipropylenetriamine, bis(hexamethylene)triamine and bis(aminopropyl)piperazine with

(ii) a crosslinker selected from the group consisting of epichlorohydrin, bischlorohydrinethers of C2- to C6- alkylene glycols, bischlorohydrinethers of polyethylene glycols having 2 to 14 ethylene glycol units, trischlorohydrinether of trimethylolpropane, trischlorohydrinether of glycerol, tetrachlorohydrinether of pentaerythritol, bisglycidylether of ethylene glycol, bisglycidylether of polyethylene glycols having 2 to 14 ethylene glycol units, trisglycidylether of trimethylolpropane, tetraglycidylether of pentaerythritol, urea, melamine, adipic acid, terephthalic acid, phthalic acid, α,ω-dodecanoic acid and hexamethylene diisocyanate.

7. A process for the production of zwitterionic polyamines which comprises

(a) reacting

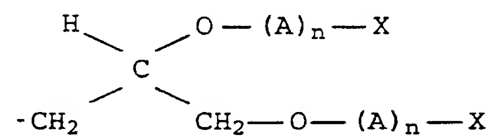
(i) an aliphatic or araliphatic monoamine or a polyamine containing 2 to 5 primary, secondary or tertiary nitrogen groups with

(ii) a crosslinker selected from the group consisting of epihalohydrins, polyglycidyl ethers with 2 to 4 glycidyl groups, polyhalohydrins with 2 to 4 halohydrine groups, dicarboxylic acids, their esters chlorides, amides or anhydrides, diisocyanates, urea and melamine,

in a ratio (i) : (ii) of from 20 : 1 to 1 : 1 with reference to molar amounts of amino groups in the amines of (i) and molar amounts of reactive groups in the crosslinker of (ii), resulting in the formation of a crosslinked polyamine having a molecular weight of from 150 to 1,500,

(b) alkoxylating the crosslinked polyamine obtained according to step (a) with at least one C2- to C4-alkylene oxide or tetrahydrofurane at such a ratio that on each NH group of the crosslinked polyamine 1 to 50 units of the alkylene oxide are added,

(c) reacting the alkoxylated polyamine obtained according to step (b) with a compound selected from the group consisting of halogen sulfonic acid, halogen phosphorous acid, vinyl sulfonic acid, propane sultone, halogen acetic acid, acrylic acid, methacrylic acid, vinyl phosphorous acid, and the alkali metal or ammonium salts of the said acids in such a manner that at least one tertiary amine end group of the alkoxylated crosslinked polyamine contains two groups having the formula

$-(A)_n-X$ (I) or  (II)

wherein

A means an ethylene oxide unit, a propylene oxide unit, a unit of butylene oxides and a tetrahydrofuran unit,

n is a number of from 1 to 50,

X is $-SO_3M$, $-CH_2-CH_2-SO_3M$, $-CH_2-CH_2-CH_2-SO_3M$,

$-CH_2-CH(OH)-CH_2-SO_3M$,

$-CH_2-COOM$, $-CH_2-CH_2-COOM$,

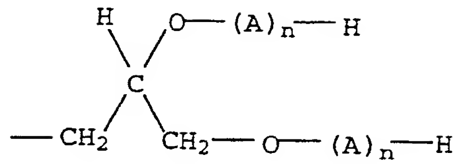
$-PO_3M_2$, $-CH_2-CH_2-PO_3M_2$,

with the proviso that in formula II one X may also be hydrogen and

M is hydrogen, alkali metal or ammonium,

or containing one group of formula I or II and one group selected from radicals consisting of

$—(A)_n—H$,



C_1- to C_{22}-alkyl and C_7- to C_{22}-aralkyl, the meaning of A and n is the same as in formula I or II,

and optionally

(d) quaternizing up to 100% of the tertiary nitrogen atoms of the reaction product obtained according to step (c), or quaternizing the reaction product obtained according to step (b) and subsequently carrying out the reaction according to step (c).

8. A process as claimed in claim 7, wherein the alkoxylated crosslinked polyamine obtained according to step (b) is quaternized up to 100 % and subsequently reacted with chlorosulfonic acid.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/06294

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G65/32 C08G65/26 C11D3/37

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	WO 97 42285 A (GOSSELINK EUGENE PAUL ;WATSON RANDALL ALAN (US); MANOHAR SANJEEV K) 13 November 1997 (1997-11-13) claim 1 examples 1-4 ---	1-8
A	EP 0 111 976 A (PROCTER & GAMBLE) 27 June 1984 (1984-06-27) cited in the application claim 1 page 18 ---	1-8
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

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Date of the actual completion of the international search	Date of mailing of the international search report
14 November 2000	24/11/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	O'Sullivan, T

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INTERNATIONAL SEARCH REPORT

Inte ional Application No
PCT/EP 00/06294

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 4 686 050 A (HOWERIN CHARLES) 11 August 1987 (1987-08-11) claim 1	1-8
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A	EP 0 553 575 A (HERCULES INC) 4 August 1993 (1993-08-04) claims 1,2	1-8

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Information on patent family members

International Application No
PCT/EP 00/06294

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